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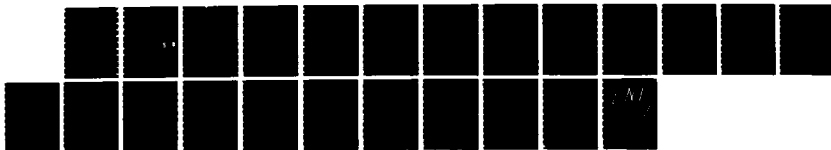
PHASE DIAGRAMS FOR THE PEO-LIX ELECTROLYTE SYSTEM(U)
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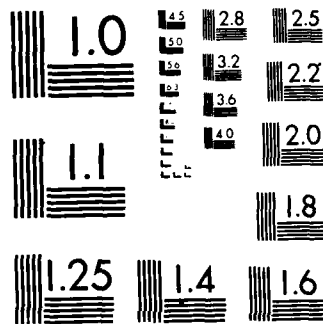
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Phase Diagrams for the PEO-LiX Electrolyte System

by

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PHASE DIAGRAMS FOR THE PEO-LiX ELECTROLYTE SYSTEM

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ABSTRACT

The phase diagrams for the PEO-LiX (X = AsF_6 , CF_3SO_3 , BF_4 , PF_6 and AlCl_4) systems have been constructed from differential scanning calorimetry (DSC) measurements. The results confirm that the systems are multi-eutectic multi-phased and that the stoichiometries of the intermediate compounds are not fixed at any single ratio such as 4:1 O/Li.

1. INTRODUCTION

Fast ion conduction at 100°C on solid polymer electrolytes based on polyethylene oxide (PEO) has been reported by Fenton et al (1). These results led to the first use of such polymer electrolytes in a solid state electrochemical battery (2) and especially stimulated the recent developments of all-solid state lithium batteries. The attractive mechanical and electrical properties ($\sigma \sim 10^{-4} - 10^{-3} (\Omega\text{cm})^{-1}$ at 100°C) of these polyether complexes resulted in further investigations on ionically conducting polymers (3).

The complexes formed between PEO and various alkali metal salts (MX) have been a matter of debate over the last few years. It has been shown that many of these ionically conducting materials are not single phase and phase diagram investigations reveal the presence of more than one compound (4,5,6). It has also been shown for the PEO- LiBF_4 system that allotropes exist depending upon the solvent used (7).

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Numerous studies have been made on these alkali metal complexes with regard to their structure, stoichiometry and transport properties. A polyhelical structure for these complexes has been proposed (8) and recent x-ray data (9) indicate the cations to lie outside the helical channels as opposed to the previously accepted structure where they were surrounded by the oxygen lone pairs from the PEO. Hence the ionic transport mechanism is expected to be quite complex. Pure PEO has a glass transition temperature (T_g) of -60°C . The material is highly crystalline ($>60\%$) and melts at 71°C . The alkali metal complexes have been shown to be inhomogeneous and below 71°C , three phases coexist, the crystalline PEO phase, the crystalline complex and the amorphous phase.

Weston and Steele (10) measured the a.c. conductivity on a number of lithium salt-PEO complexes and correlated their results with DSC analysis. The increase in the observed conductivity above 150°C was explained by the melting of the crystalline polymer complex in the elastomeric phase. Recent NMR results indicate the ionic conductivity to be associated with the elastomeric phase (11). The stoichiometry of these complexes may be related to the polyhelical structure. In most cases, the O:M ratio of 4:1 has been found with some occurrences of 8:1 and 3:1. This indicates that the stoichiometries are not well known and several factors can account for this. The investigation of these materials is thus quite complex because of their indifferent behaviour. Different stoichiometries could result depending upon the method of preparation and in particular upon the sample's thermal history (10). Much has been published on this last aspect with quite ambiguous results (12,13). It appears from previous findings that the formation of the crystalline complex is imperative before any investigation be carried out. This can be accomplished by heating and cooling the the polymer-salt product to $50-150^\circ\text{C}$ and allowing sufficient time to crystallize. The initial part of this work involved the study of the recrystallization kinetics on a known system (PEO- LiCF_3SO_3) before obtaining the DSC thermograms on our samples.

Phase diagrams for a number of alkali metal salt-PEO systems have been established (4,5,6,14-17). One of the important features

of these phase diagrams has been to show the presence of one or more intermediate compounds which are subsequently characterized by one or more eutectic reactions. For the PEO-NaSCN system (14) the stoichiometry of the intermediate complex has been shown to be $(\text{PEO})_3\text{NaSCN}$ as it is for the PEO-NaI system (15). However complexes formed between PEO and a lithium salt indicate slightly higher stoichiometries of the intermediate compounds (eg 3.5:1 for PEO- LiCF_3SO_3 (15) and 3.4:1 for PEO- LiBH_4 (18)).

Our study involves the use of DSC measurement to establish skeleton phase diagrams for the PEO-LiX systems (where $X = \text{CF}_3\text{SO}_3$, AsF_6 , BF_4 , PF_6 and AlCl_4). The phase diagrams for the LiAsF_6 and LiCF_3SO_3 salts complexed with PEO has recently been presented by Robitaille and Fauteux (6) using optical microscopy and x-ray studies. Subsequent studies will involve the use of x-ray diffraction and conductivity measurements to establish and correlate the stoichiometries of the intermediate compounds.

2. EXPERIMENTAL

2.1 Preparation of Polymer-LiX mixtures.

Polyethylene oxide (PEO) of molecular weight 5×10^6 was supplied by Polysciences in powdered form. The material was dried at 50°C for several days prior to its use. The lithium salts were dried at the temperatures specified below; LiCF_3SO_3 (3M) at 50°C for several days, LiAsF_6 (Alfa) used as received, LiBF_4 (Alfa) 50°C for 24 hrs, LiAlCl_4 (Lithcoa) used as received and LiPF_6 (Ozark) 50°C for 24 hrs. All subsequent handling of the materials was carried out in a $<1\%$ RH dry room. All of these lithium salts and the PEO dissolve fairly easily in acetonitrile and films were cast from this solvent.

To form the films, known weights of the appropriate salts were dissolved in acetonitrile. To this solution, known weights of PEO were added slowly with constant stirring. A typical preparation would be, 0.554g LiCF_3SO_3 dissolved in 25ml acetonitrile followed by 1.25g PEO. In the case of low salt compositions, the solution was homogeneous within a few minutes. However higher salt concentrations gave lumpy precipitates and these were subsequently stored in sealed

bottles for 2-5 days at 50-100°C to homogenize. The final solutions were without precipitates.

Large areas of bubble free films were cast onto Halar sheets in a dry room fume^hood using the doctor blade technique. The films were air-dried in the dry room for several days prior to storing. The films prepared in this way had variable flexibility and opaqueness. The higher salt content films were brittle and opaque as expected. The thickness of the films varied between 10 and 20 μm . Films of these low thicknesses dried under the above conditions appeared satisfactory with regards to the removal of the solvent acetonitrile. Once dry and solvent free, the electrolyte films were stored in sealed bags for 2 months to allow complete crystallization of the complex.

2.2 DSC Analysis

The thermal analysis of the samples were studied using a Mettler DSC 30 differential scanning calorimeter. The samples were weighed in a DSC pan and hermetically sealed using the supplied crimper. The samples were studied over the temperature range of -150°C to +350°C at a constant heating rate of 5°C per minute. The DSC traces were analyzed using a TC10-TA Processor in conjunction with a Print Swiss Matrix printer. The enthalpies of transition were obtained directly using this method.

The commonly used composition $(\text{PEO})_8.\text{LiCF}_3\text{SO}_3$ was analyzed to study its recrystallization kinetics. This subject is rather ambiguous in the literature and we investigated this on the samples prepared in the above manner. This involved treating the samples in different ways and obtaining the DSC traces during the heating cycles from 25° to 250°C. The following conditions were used:

- (a) freshly prepared films were heated to 250°C, cooled down to 25°C and immediately reheated.
- (b) freshly prepared films were heated to 250°C, cooled down to 25°C and reheated after 2 days.
- (c) films that were 2 months old were heated to 250°C, cooled down to 25°C and immediately reheated.

(d) films that were 2 months old were heated to 250°C, cooled down to 25°C and reheated after 2 days.

3. RESULTS AND DISCUSSION

3.1 Recrystallization Kinetics

Figure 1a - 1d shows the DSC traces for the conditions given above. In all cases two endothermic peaks occur indicating that two crystalline phases coexist at room temperature; a pure PEO peak which melts between 58-60°C, and an intermediate salt rich crystalline compound that dissolves in the elastomeric phase.

Figure 1a shows that very little change in the peak areas occurs during the first heating and the second heating immediately after cooling. Figure 1b was also on a freshly prepared film and the first heating cycle was the same as in Figure 1a, but after cooling the sample was allowed to remain at room temperature for 2 days. On further heating, the DSC trace was indifferent. The peak temperatures were the same, but the peak areas had decreased during the melting of the PEO and increased during the melting of the intermediate compound. This suggests that during the lapsed time there occurs a considerable redistribution of the lithium salt within the polymer and recrystallization of the crystalline intermediate.

Figure 1c shows a DSC trace of an electrolyte material that had been allowed to stand for 2 months in the dry room. During the first heating cycle a considerably smaller melting peak was obtained for PEO than that observed in Figure 1a or 1b, followed by a correspondingly larger peak for the intermediate complex. However heating the sample immediately after cooling resulted in an increased PEO peak area whereas that for the complex decreased. This suggests that during the cooling, crystallization of the complex was incomplete. Figure 1d shows a trace where a sample was heated and allowed to cool at room temperature for 2 days. Further heating results in a trace similar to the first heating. The peak areas are summarized in Table 1 in terms of the heat of transition for the above cases. We conclude from these results that for crystallization to be complete, the sample must be

- (1) heated and cooled to room temperature and allowed to stand for sufficient length of time (~ 2 days) or
- (2) allowed to age.

The above results indicate that recrystallization can be increased if the sample is first heated to +150°C. However the time of recrystallization can vary considerably in samples containing a larger salt content or in samples that may have two or more intermediate compounds. The preferred route would be to allow the samples to age. This was the procedure adopted in determining the subsequent phase diagrams.

TABLE 1

Sample	$\Delta H/Jg^{-1}$ of PEO on 1st heating	$\Delta H/Jg^{-1}$ of PEO on 2nd heating	$\Delta H/Jg^{-1}$ of complex on 1st heating	$\Delta H/Jg^{-1}$ of complex on 2nd heating
Freshly prepared $(PEO)_8$. $LiCF_3SO_3$ corresponding to Figure 1a	66.23	67.18	15.20	15.82
Freshly prepared $(PEO)_8$. $LiCF_3SO_3$ corresponding to Fig. 1b	65.39	62.14	14.86	21.62
Aged $(PEO)_8$. $LiCF_3SO_3$ corresponding to Fig. 1c	60.94	65.02	30.53	19.50
Aged $(PEO)_8$. $LiCF_3SO_3$ corresponding to Fig. 1d	60.74	55.83	31.22	30.83

3.2 Phase Diagrams

The phase diagrams for only three lithium salts complexed with PEO has been published (LiCF_3SO_3 , LiClO_4 and LiAsF_6). The most extensively studied salt has been LiCF_3SO_3 . In this paper we have constructed skeleton phase diagrams for five $\text{LiX} \cdot \text{PEO}$ complex systems. Besides confirming the composition range of some of the previous studies, the new compositions were also characterized.

3.2a PEO - LiCF_3SO_3 System

Figure 2 gives the phase diagram for the PEO- LiCF_3SO_3 system. The diagram was constructed between the values of one and fifty for the atomic ratio of O/Li. Previously published results did not report on the range from 3 down to 1. The transition temperatures on the diagram include data from other sources using NMR(15), DSC(10,12), DTA(7), a.c. conductivity (10,12,6), and optical microscopy(6,19). Our results are in excellent agreement with previous data. The diagram shows that below the eutectic temperature ($\sim 67^\circ\text{C}$), three phases can exist, (amorphous phase plus the two crystalline phases). Beyond the melting point, the solid complex begins to dissolve in the elastomeric phase. At O/Li ratios lower than 3, a second intermediate compound results. This material also appears to be a three phase system below the higher eutectic temperature ($\sim 170^\circ\text{C}$), i.e., two intermediate compounds and an elastomeric phase. The subsequent intermediate compound results from a reaction between the excess lithium salt and the first complex salt.

In order to explain the observed stoichiometries for the various systems, it is important to understand the structure and transport properties of the material. The previously assumed 4:1 stoichiometry of the $\text{PEO} \cdot \text{LiCF}_3\text{SO}_3$ complex had been based on the usually accepted helical structure where the cations are surrounded by the PEO strands. This concept involves the conduction of cations from site to site along the core of the helix. However, experimental results contradict this arrangement of cations. The 4:1 "fixed" stoichiometry is invalid with salts such as NaBH_4 which tend to give more concentrated complexes (20). Under these conditions the

mobility of the cations would be seriously impaired. Lattice parameter data (9) suggest that the alkali ions are situated outside the polymer helix. A new approach (8) has been put forward such that at $T > T_m$, the excess PEO in the mixture reacts with the concentrated intermediate compound to give a more dilute complex. This occurs because the alkali ion situated outside the helix coordinates with the oxygen lone pairs available from the excess PEO. The conduction of cations in this case can thus occur via these lone pairs. This approach can at least explain the over-stoichiometries observed for some of the intermediate compounds (15). The result is a relatively unsaturated complex with respect to the cation. The effect is to remove the overall strain on the system.

Our analysis of the stoichiometric composition was based on the relative heats of fusion of excess crystalline PEO in the $(\text{PEO})_n\text{-LiX}$ system (9). As shown in Figure 3, the composition at which this heat of fusion equals zero identifies the stoichiometry of the intermediate compound. In the case of LiCF_3SO_3 , this suggests a stoichiometry of 3.3 oxygen per lithium for the first intermediate compound. This is in reasonable agreement with the work of Berthier et al. (1). The stoichiometry of the subsequent intermediate compounds are extremely difficult to analyze by the above technique and will not be attempted here. Other techniques such as x-ray diffraction and conductivity measurement are suggested and this work is currently in progress.

Beyond the 50:1 ratio for O:Li we detect the presence of the eutectic point. This appears to occur somewhere between 200:1 and 100:1 O/Li ratio and is in agreement with results of Robitaille and Fauteux (6). A second eutectic was detected in the higher salt concentration region and is characterized by the melting of the two intermediate compounds.

3.2b PEO-LiAsF₆ System

The phase diagram for the PEO-LiAsF₆ system is shown in Figure 4. The diagram includes the various phase-transition temperatures obtained by microscopy and conductivity measurements (6). Our result in the low salt concentration region is in reasonable agreement with

the previous data. These workers have detected a second intermediate at composition below 6:1 O/Li ratio. Wide angle x-ray scattering and polarized light optical microscopy were used to determine the phase diagram and stoichiometry of the intermediate compounds. This suggests the formation of two intermediates with composition $(\text{PEO})_6 \cdot \text{LiAsF}_6$ and $(\text{PEO})_3 \cdot \text{LiAsF}_6$. Other intermediates are known to occur but their stoichiometry is not given.

The present results suggest a stoichiometry of $(\text{PEO})_{6-6.4} \cdot \text{LiAsF}_6$ for the first intermediate compound formation. At higher salt concentration other solid complexes result. The stoichiometries of these intermediates will be analyzed using x-ray diffraction. The diagram shows that the first eutectic composition occurs at an O:Li ratio of 21:28:1 [cf ref. 6]. This results from the interaction between pure PEO and $(\text{PEO})_{6-6.4} \cdot \text{LiAsF}_6$. Furthermore the liquidus line for the second intermediate compound (O:Li < 6:1) is rather flat, in sharp contrast to previous results.

3.2c PEO-LiBF₄ System

Pure PEO forms complexes with LiBF₄ and the subsequent phase diagram for this system is shown in Figure 5. There has been no previous publication of the phase diagram for this system. However Payne and Wright did study this mixture and their TGA data showed that the complex formed between PEO and LiBF₄ melted at different temperatures depending upon the type of solvent used to cast the electrolyte (7). Furthermore the stoichiometry of the intermediate compound was reported to be 4:1 (O:Li). Our DSC result suggest that the system is once again multiphase and that the stoichiometry of the first intermediate compound is 2.5:1 (O:Li). This has been deduced from the heats of fusion of excess crystalline PEO (Figure 3). A second intermediate forms at O:Li ratio of <2.5:1.

The eutectic formation between PEO and $(\text{PEO})_{2.5} \cdot \text{LiBF}_4$ occurs between O:Li ratios of 20:1 and 16:1. The system appears to have the same basic pattern as the two previous systems studied. However the stoichiometries have been quite different. This is reflected in the relatively high solubility and low crystal lattice energy which favors ionization of the LiBF₄ in PEO (21). This is also confirmed

by the first eutectic point composition $(\text{PEO})_{16-20} \cdot \text{LiBF}_4$, which has a higher salt concentration than the $\text{PEO-LiCF}_3\text{SO}_3$ [$(\text{PEO})_{100-200} \cdot \text{LiCF}_3\text{SO}_3$] or PEO-LiAsF_6 [$(\text{PEO})_{21-28} \cdot \text{LiAsF}_6$] system. Again a rather flat liquidus line is suggested for the melting of the second intermediate compound.

3.2d PEO-LiPF₆ System

The phase diagram for the PEO-LiPF_6 system is shown in Figure 6. The diagram is somewhat different from the three previous phase diagrams. The system appears quite complex with multiple phase formation. The first eutectic point forms between PEO and the first intermediate at the O:Li ratio of 22-28:1. The first eutectic temperature occur at 62.5°C while the second and third eutectic temperature occurs at 117° and 188°C respectively. The system appears to form second and subsequent intermediate compounds with relatively high melting points.

The formation of the first intermediate compound occurs at O:Li ratio of 6.2:1. At lower salt concentration the system shows a distinct similarity with the PEO-LiAsF_6 system in that the stoichiometry of the first intermediate compound is about 6:1(O:Li). The system is thus isomorphous up to a salt concentration of 6:1(O:Li).

3.2e PEO-LiAlCl₄ System

Figure 7 shows a tentative phase diagram for the PEO-LiAlCl_4 system. The unusual behaviour at such low temperatures is explained by the fact that LiAlCl_4 decomposes without melting at about 150°C . Furthermore it appears to us that below the melting point of PEO, the system is three phase throughout the composition studied. Two reasons could be given to explain this. Either LiAlCl_4 is still appreciably soluble at O:Li ratios of 1:1 in which case there is still a measurable amount of crystalline PEO to give a peak during the DSC scan, or LiAlCl_4 has partially dissociated as LiCl and AlCl_3 in PEO in which case there may still be excess crystalline PEO to be reacted with LiAlCl_4 . In the former case, the stoichiometry of the intermediate compound is expected to be at a much higher salt

concentration. If the latter is true then this explains the crystalline PEO melting peaks observed at all salt concentration. On the other hand both phenomena could be occurring. X-ray data will probably shed more light as to the validity of this particular system.

4.0 CONCLUSION

Crystallization studies suggest that PEO-alkali metal salt complexes need not be heated at elevated temperatures for crystallization of the intermediate compounds to occur but can be left to age at ambient temperatures. DSC measurements were made on these polymer electrolytes to investigate the phase diagrams of the LiX-PEO systems (X = CF₃SO₃, AsF₆, PF₆, BF₄, and AlCl₄). The stoichiometry of the intermediate compounds as determined from the relative heats of fusion of crystalline PEO indicated variable stoichiometry for the different salts complexed with PEO.

ACKNOWLEDGEMENT

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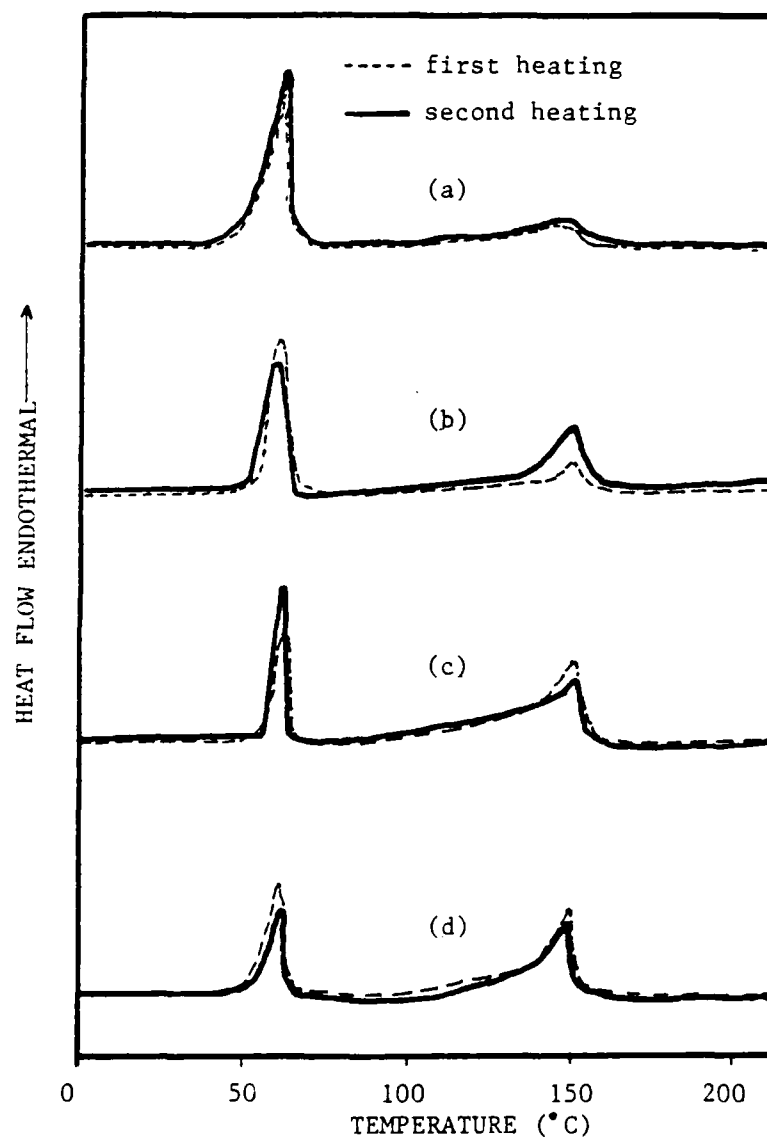


Figure 1. DSC traces for $(\text{PEO})_8 \cdot \text{LiCF}_3\text{SO}_3$,
heating rate--- 5 /minute.

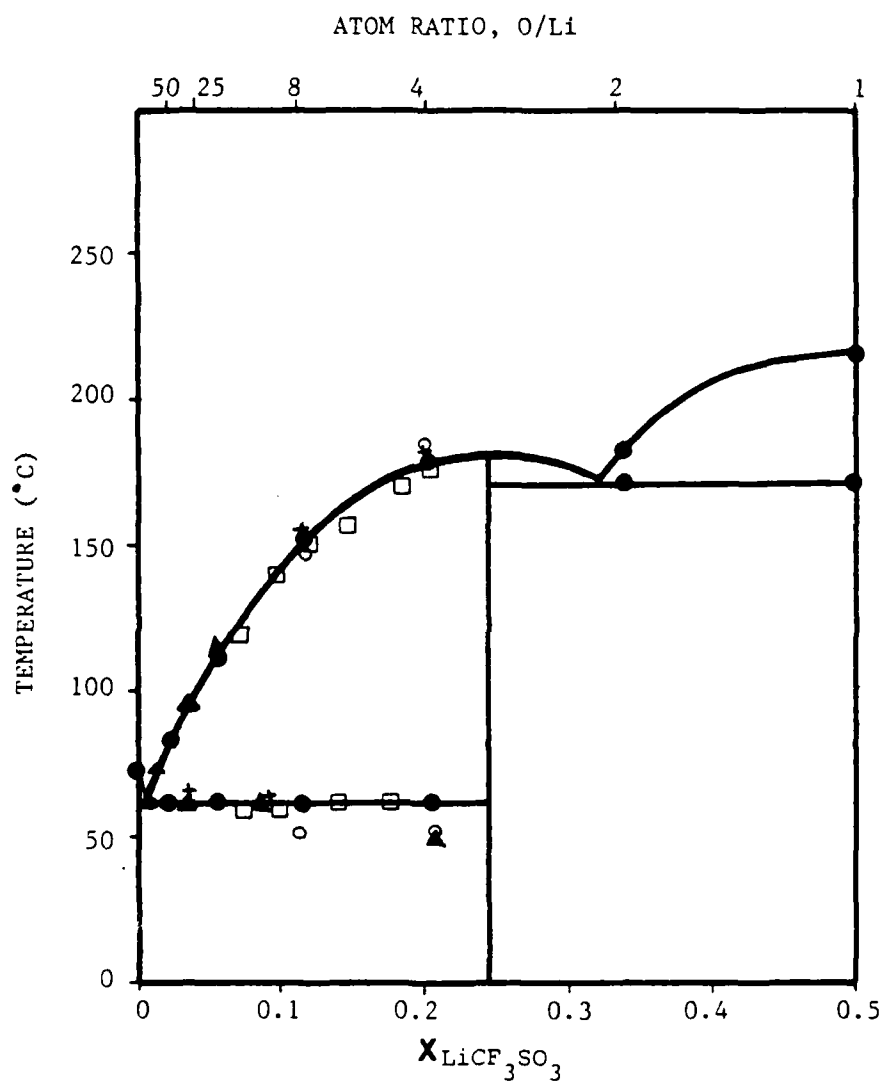


Figure 2. Phase diagram of the PEO-LiCF₃SO₃ system
 ● —this study; ○ —NMR(15); □ —DSC or DTA(7, 10,12); ▲ —a.c.conductivity(6,10,12); + — optical microscopy(6).

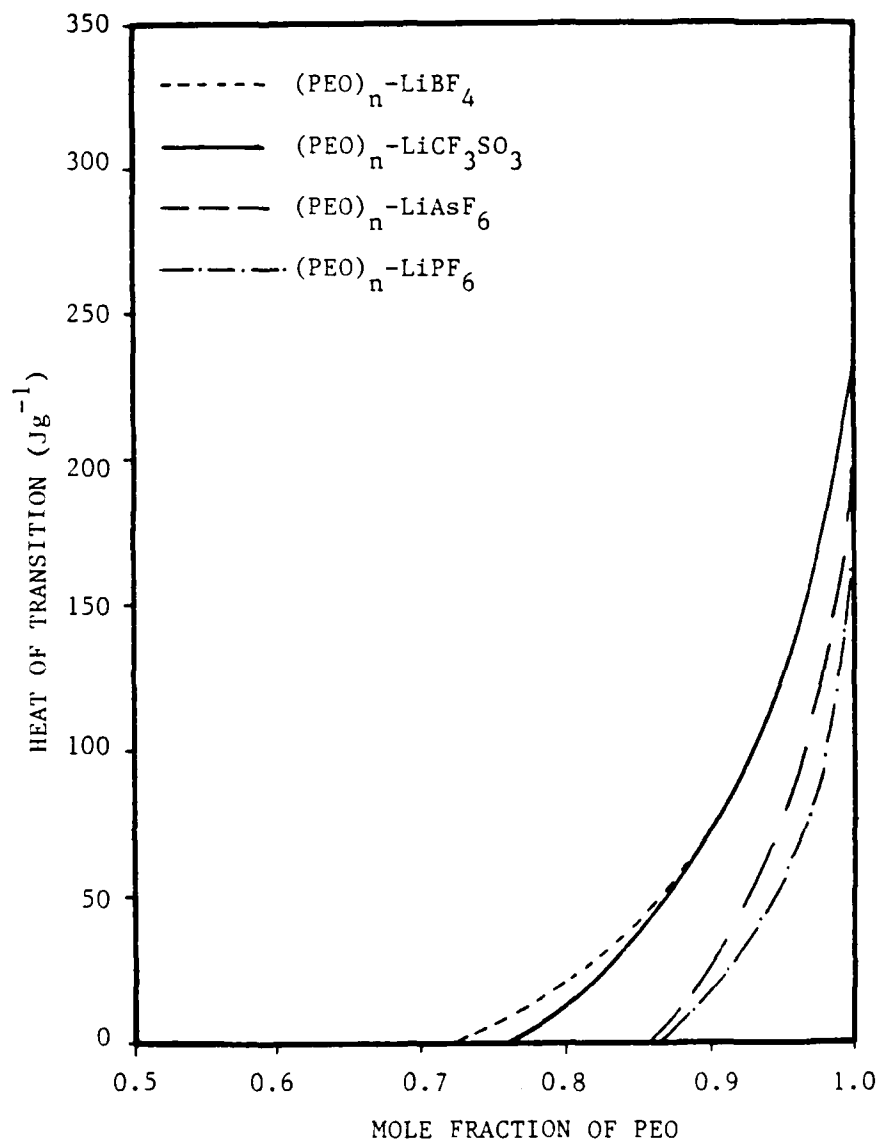


Figure 3. Heat of fusion of excess crystalline PEO in (PEO)_n-LiX samples.

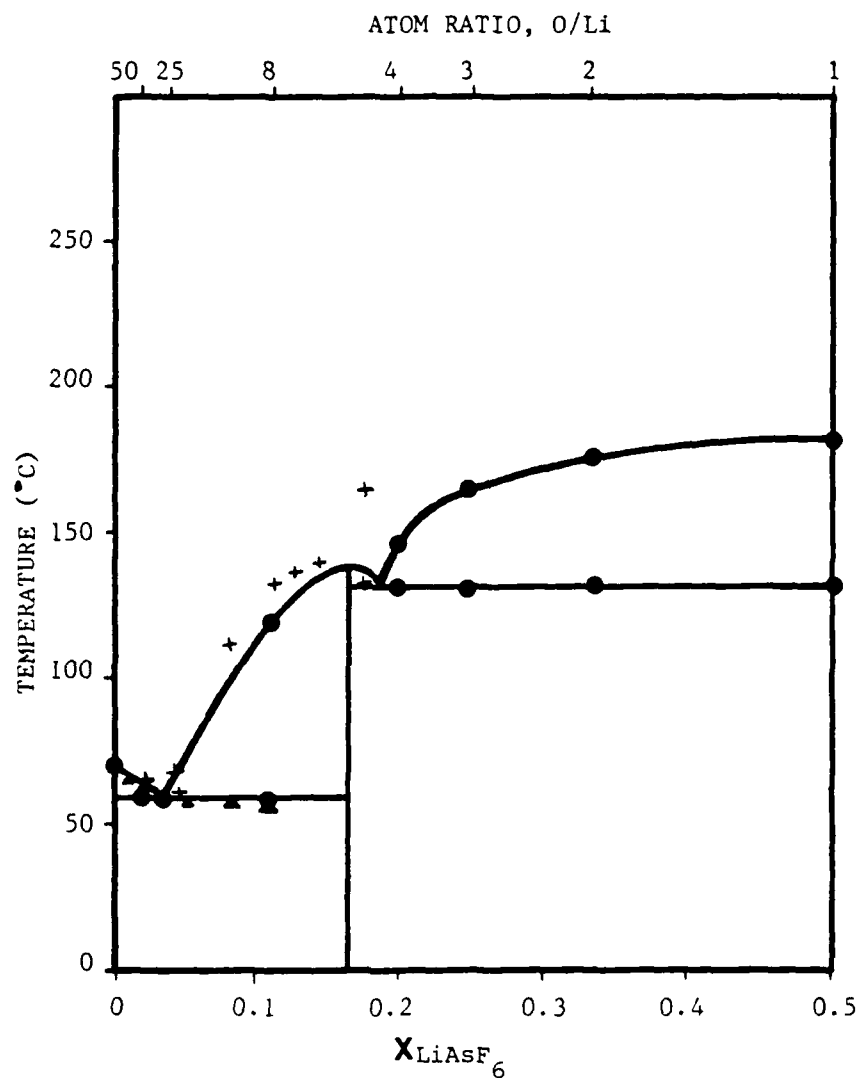


Figure 4. Phase diagram of the PEO-LiAsF₆ system.

● —this study; + —optical microscopy(6);
 ▲ —a.c.conductivity(6).

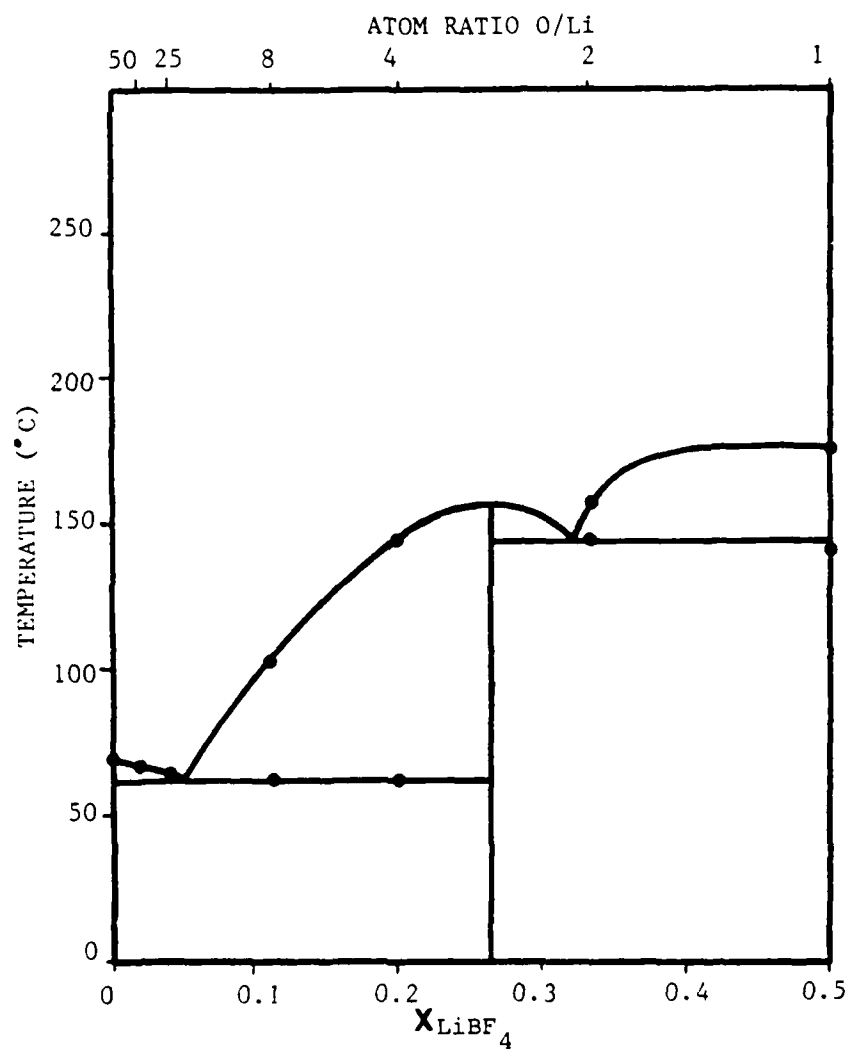


Figure 5. Phase diagram of the PEO-LiBF₄ system

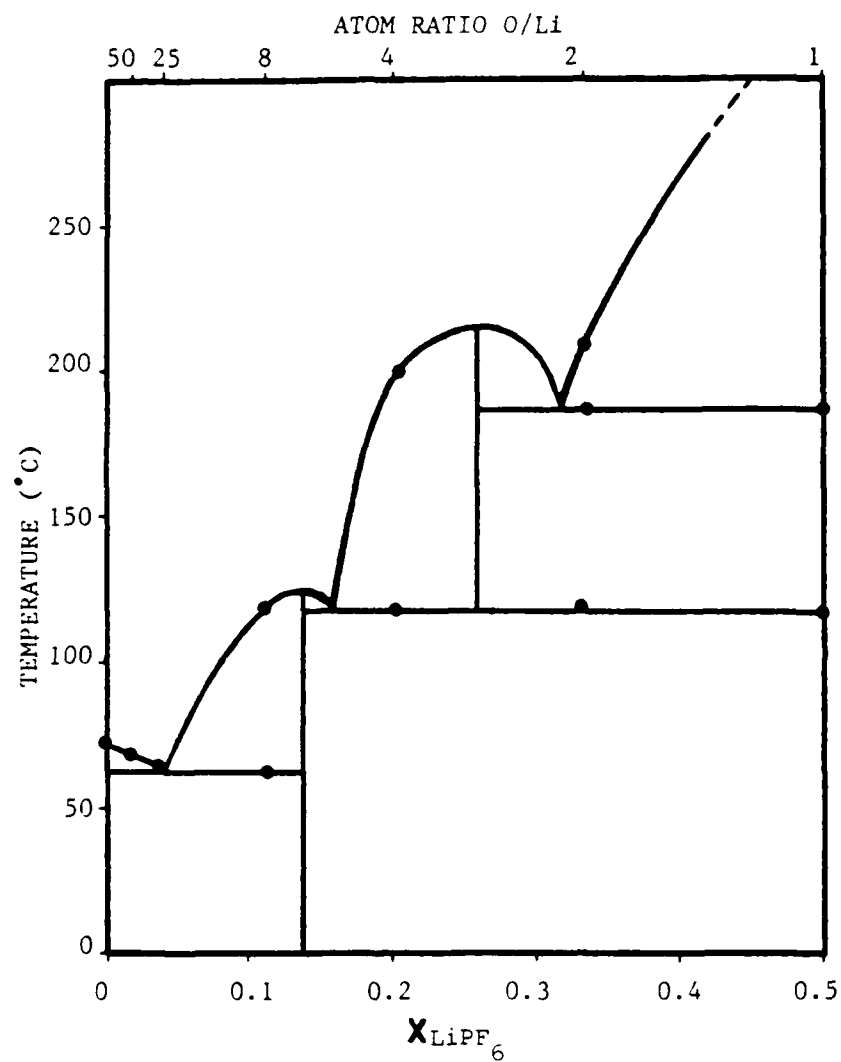


Figure 6. Phase diagram of the PEO-LiPF₆ system.

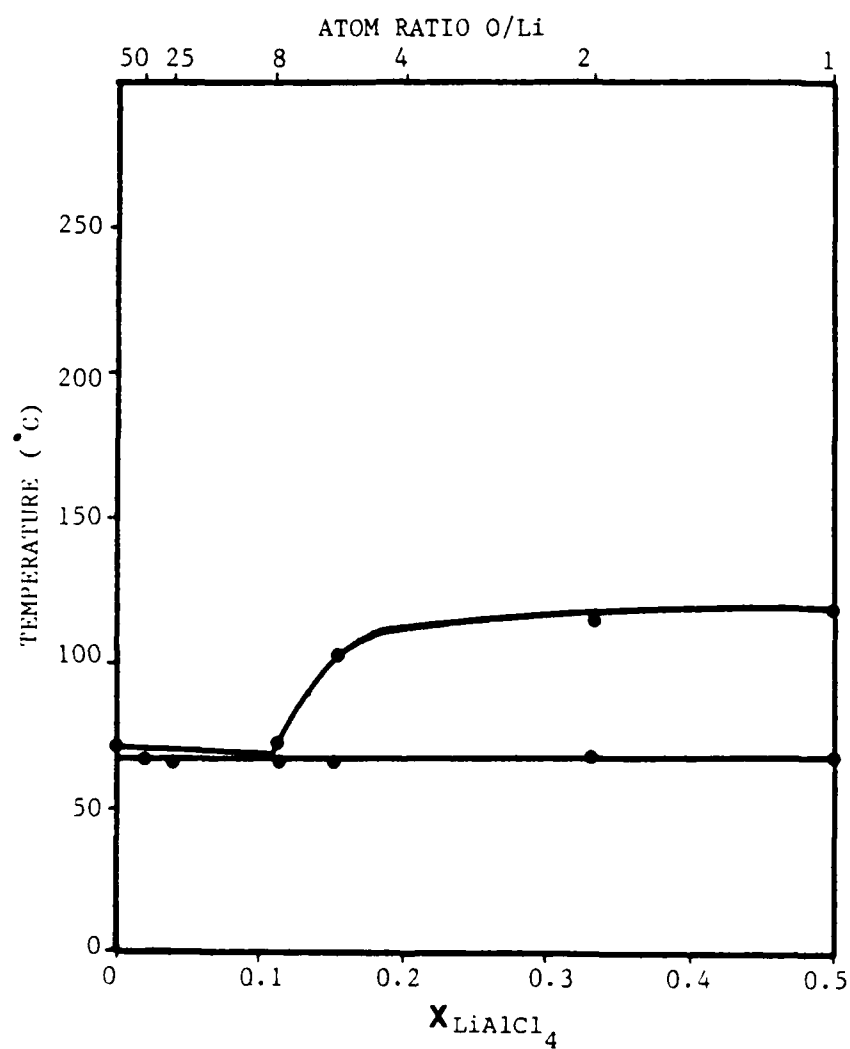


Figure 7. Phase diagram of the PEO-LiAlCl₄ system.

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